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LAND TREATMENT FIELD STUDIES

Volume 5. Wastewater Treatment Sludge from Batch Organic Chemical Synthesis

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16. ABSTRACT

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report provides the results of a field study investigation of one of six sites receiving industrial waste sludges by land cultivation. The purpose of the study was to identify and verify parameters which lead to environmental acceptability of the waste, and to recommend research needs for establishing guidelines and criteria for land cultivation.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report presents the results of field measurements and observations of a land treatment operation using a sludge generated from organic chemical manufacture. The sludge is applied to a turf farm which contains acidic soil; the sludge reduces the lime addition requirements for pH adjustment. The subsoils are porous and the quality of the groundwater located at 20-30' below the ground surface is pristine.

The site was sampled once. Observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

Results indicate increased levels of copper in the application area soils and grass compared to controls. There is little monitoring and record keeping at the site. Furthermore, the responsibilities of the waste generator do not overlap with those of the turf farmer so that waste application rates are not based on waste composition. For these reasons, further study is recommended to determine waste migration and organic degradation at the site.

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SECTION 1

INTRODUCTION

Land treatment is the application and incorporation of solid or semi-solid waste into surficial soils. Other terms used to describe this practice include land farming, land cultivation, refuse farming, land spreading, soil farming and soil incorporation. The term land application, on the other hand, usually refers to irrigation of surficial soil with wastewater. Land treatment is essentially a physical/chemical/biological waste treatment method that utilizes the natural capacity of the soil system to aerobically degrade, assimilate and immobilize certain waste constituents.

At every land treatment site, there is a dynamic balance of decomposition, attenuation and migration of waste constituents. The extent to which any one of these mechanisms occurs depends on the waste character, site character and cultivation procedures.

A land treatment site should provide decomposition of the organic constituents applied and incorporated. The migration of soluble constituents from a land treatment site should be within environmentally acceptable concentrations for the receiving media, particularly ground and surface waters. The attenuation of remaining constituents over the design life of the site should not lead to a build up of total concentrations that could harm the soil structure, cause phytotoxicity, or lead to excessive concentrations in the food web through bioaccumulation.

From the above discussion, it is evident that specific site characteristics and waste characteristics together are key to achieving environmentally optimal use of surficial soils in waste treatment. Equally important (although not as evident) is the management of the land cultivation operation; no matter how optimal conditions may be for degradation/attenuation of waste, some sites can be overloaded. Management of a site can be viewed as the means through which desired waste treatment conditions are maintained.

OBJECTIVES

The objective of this project was to identify parameters which contribute to (or affect) the environmental acceptability of land treatment of a wastewater treatment sludge from organic chemicals synthesis on a turf farm. The parameters are classified by waste characteristics (e.g., percent solids, salt content), site characteristics (e.g., topography, climate) and landfarm management procedures (e.g. soil aeration, frequency of waste application). Environmental acceptability was determined by significant increases in waste constituents in the application soils compared to controls and by the potential for environmental contamination due to a combination of waste, site and management parameters.

DESCRIPTION OF THE SITE

The identity of this site is protected by a confidentiality agreement included as part of the contract for this study. The site is a turf farm which has been utilized for land treatment sludge generated from batch organic chemical manufacture since 1976.

Waste Characteristics

The wastes at this site represent combined wastewater treatment sludges from clarifier and activated sludge lagoons of an organic chemical manufacturing facility (SIC Code 2865). The sludges are pumped to a 500,000 gallon concrete lined lagoon that is equipped with aerators. Aeration prevents anaerobic conditions (and attendant odors) in the lagoon. About six million gallons of sludge (7% solids) are generated annually of which two-thirds is disposed of by landfill. The remainder is sent to the turf farm. For the waste generator, this presents a low-cost (in terms of equipment purchases) disposal option; for the turf farmer, the waste is a supplementary source of lime and a beneficial soil amendment.

Site Characteristics

The site is located in an area of prime agricultural soils for its region (Table 1). Approximately three feet of silt loam (it can be less in some areas) covers stratified sand and gravel. As a result, the available water capacity is high in surface soils but low in underlying strata, with the reverse being true for permeability. The flooding of surface soils seems of low probability (except when frozen) due to the high permeability of the subsurface strata so close to the surface.

Natural soils in this area tend to be acid (leached), typically requiring pH amendment for agricultural production. The cation-exchange capacity was observed to be in the low-moderate range in soils sampled from areas where wastes had not been applied. Without pH amendment (which affects both CEC and availability of certain metals) these soils would be considered moderately good at best in terms of their assimilative capacity for metals such as zinc and copper. Assimilative capacity is especially important at this site as surface soils are relatively shallow and are underlain by porous material.

Groundwater monitoring wells were not available for sampling at this site. According to published sources, groundwater is located at about 20 to 30 feet below grade; state officials have identified the groundwater as being of principal importance as a drinking water source. According to farm site personnel, an existing well for irrigation and drinking water use was dug to 55 feet. A small stream borders the site to the south, and is separated from the nearest known application areas by a minimum of about 100 feet of well-vegetated riparian cover. The stream is even further removed from most of the application locations. For these reasons, it is unlikely that the groundwater or surface water will come into direct contact with the waste.

TABLE 1. SELECTED PHYSICAL/CHEMICAL CHARACTERISTICS OF THE SITE

Characteristics	Published Source*	Data From Site Visit/ Analysis**
I. Soil		
A. Soil Classification	Approximately top 3 feet are silt loam; underlain by stratified sand and gravel	Same
B. pH Characteristics	Approximately 4.5-5.2 for non-amended soils	5.0 to 5.7 (control area)
C. Cation Exchange Capacity (meq/100g soil)	-	6.1 to 10.2 (control area)
D. Soil Organic Content (or TOC)	-	TOC: 2.92% dry solids (control area)
E. Water Retention Ability	a) Surface layers have high available water capacity; low for sub-surface sand and gravel b) Permeability: approximately 0.6 to 2.0 inches per hour in surface layer; >6 inches per hour in sand/ gravel	Surface puddles observed when ground still frozen
II. Ground & Surface Water Proximity		
A. Surface Water	Small stream to south	Site Visit Observation** Small stream ~100 to 1000 feet from application areas
B. Ground Water	20-30 feet to groundwater	Local well for irrigation and drinking water dug to 55 feet
III. Topographical Conditions		
A. General Topography of Vicinity (Published Source)*	-	-
B. Topographic Relief of Areas Visited**	Field sampled nearly level; farm area has some rises and depressions of less than 3%	-
IV. Meteorological Conditions		
A. Average Yearly Precipitation	~40 inches	
B. Typical Distribution of Precipitation	Fairly evenly distributed	
C. Frost Free Period	~200 days	
D. Temperature		
1. Summer	July ~73°F (mean)	
2. Winter	January ~29°F (mean)	

*These include information from Soil Conservation Service Publications, USGS Surveys, and/or State And University Surveys
**Interviews with facility personnel, including representatives of waste generators and farms, observations and analyses from site visits

The topography of the farm site is generally flat, with the application and control area fields being approximately level. As expected, there was no evidence of erosion since the area is covered with turf. Both rainfall and the length of the frostfree period are sufficient for agricultural production, and this crop is also irrigated. Therefore, the level of microbial activity should be sufficient to promote rapid waste degradation. During severe storm events, flooding of the stream could make surface runoff a serious problem. However, this risk is reduced since wastes are not applied in winter when the potential for flooding is higher. The site, located in a relatively rural setting, affords virtually unlimited access to indigenous wildlife. The early-successional mixed woodlands bordering the site provide excellent cover for potential use by many of the region's resident and migrant vertebrate fauna. For example, deer, fox and raptors have, on occasion, been observed by site employees. The presence of several small low areas of wetland vegetation indicates that some utilization of the area by water-dependent birds, reptiles and amphibians could take place. From the standpoint of potential human food-web interactions, at least two resident herbivores (mourning dove and rabbit) could consume vegetative matter from application areas on the site and in turn be consumed by man.

Land Treatment Site Management

Wastes landfarmed at the site are generated by an organic chemical manufacturing facility (SIC Code 2865) located 12-13 miles from the site. The wastes are residual sludges from primary and secondary wastewater treatment operations. Approximately six million gallons of sludge is produced annually by the generator. The sludge is generally about 7% solids although sludge composition may vary considerably over short time periods since production is accomplished in batch lots. Some homogeneity is achieved by pretreatment in a 500,000 gallon aerated, concrete lined lagoon prior to sending the waste off-site.

The land cultivation season runs from mid-May to early September or November depending on the weather. Within this period, application of sludge is dependent on the availability of open, harvested fields at the turf farm. When the fields are open, two tank trucks are typically used over a ten-day period during a given month. Each truck makes four to five trips per day to transport the waste the 12-13 miles to the site. Each truck is equipped with a nine-foot spreader bar. A valve is opened at the rear of the tank truck and the sludge is spread over the surface by gravity flow through the spreader bar. The amount of sludge deposited per unit area of surface land is a function of truck speed. The greatest application rate has been estimated to be 65,000 gallons per acre (personal communication from waste generator). Greenhouse experiments by a local university with site turf have suggested that up to six acre-inches of sludge ($\sim$ 150,000 gallons) can be applied with no detrimental effects on turf grass germination or growth.

Sludge is only applied to the surface of harvested, open fields. The sludge may lie on the surface for as little as one day or as long as three months; one to two weeks is typical. Incorporation of the waste into soil is carried out by turf farm personnel and equipment. The incorporation process includes the following sequence: plow harrowing (six to eight inches deep), disc harrowing (twice), lime application, reharrowing, drag screening, fertilization

and seeding. Lime applications may be reduced or eliminated as a result of waste application. Once seeded, the field will not be open for reapplication of waste or reaeration of the waste-soil mixture for 1-1/2 to 2 years (normal time period before turf harvesting). Any subsequent pH amendments (e.g., liming) and fertilizer and pesticide additions necessary for agronomic purposes are made directly on the turf.

Waste storage capability is not available at the turf farm. At present, the turf farm notifies the waste generator of the acreage that is available to receive waste and the amount of time available before such open fields will be reseeded. The waste generator then contacts the hauler, who only requires one or two day's notice. When fields are not open to receive waste and storage capacity at the generation point is fully utilized, additional sludge is disposed of by landfill.

The waste generator monitors the waste daily for selected parameters (pH is % solids, % volatile solids), and the farmer monitors soil-waste mixtures (or soil) for pH and fertilizer requirements needed to grow crops.

Table 2 summarizes the responsibility for activities surrounding the land treatment operation at the site. Clearly, the operation of the site falls into three camps - the waste generator, the hauler, and the farmer.

TABLE 2. SITE MANAGEMENT AND RESPONSIBILITY

	Plans/Decides Manages/Supervises	Performs	Approves
Storage	W.G.	W.G.	W.G.
Pretreatment	W.G.	W.G.	W.G.
Wastes Mixing	W.G.	W.G.	W.G.
Transport	W.G./F	C.H.	W.G./F
Application	W.G./F	C.H.	W.G./F
Soil Incorporation	F	F	F
Soil Waste-Amendments	F	F	F
Farming	F	F	F
Monitoring	W.G./F	W.G./F	W.G./F

W.G. = Waste Generator
F = Farmer
C.H. = Contract Hauler

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In sharp contrast to other land disposal options, land treatment can be managed so that the waste application area need not be irreversibly removed from any other potential practical usage. The basic reason is that plant-soil systems have a natural assimilative capacity for waste constituents. If rates and total quantities of wastes applied are controlled so that the assimilation capacity of the site is not exceeded for any constituent of the waste, no potential future use of the site will be precluded. Assimilative capacity is both chemical specific and site specific. In other words, each chemical constituent of a given waste will be assimilated to a different extent at the same site; and the same chemical constituents will be assimilated differently at different sites.

The conclusions of the present study are limited to the environmental acceptability of land treatment for wastewater treatment sludge from one particular batch organic-chemical manufacturing plant, at one particular application site. The results cannot be generalized, either to wastewater treatment sludges from other manufacturing plants in the chemical industry, or to other potential land treatment sites for the particular wastewater treatment sludge investigated. The field study findings do provide insight into the factors that should be considered in the design and operation of a land treatment site to ensure environmental acceptability. The field study results characterize, to the extent possible, actual practices at a land treatment site used for purposes of waste treatment rather than for purposes of research. Conditions of waste application were therefore given, and not under the control of the investigators.

CONCLUSIONS

The waste sludge as applied contained about 7% solids and 93% water. Approximately 2,000,000 gallons had been applied over a 39 acre area, two years prior to field sampling. The area had subsequently been planted with turf. Analysis of the dried waste solids showed 18% metals, 16% TOC, 3% TKN, less than 1% sulfate and chloride, and 62% undetermined. Of the metals analyzed*, only copper was found in significantly higher concentrations in the application area than in the control area. The accumulation calculated from the analytical results was 195 kg/ha. This exceeds the assimilation capacity of 125 kg/ha typical of soils with low CEC values+.

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*As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn

+M. Overcash and D. Pal, "Design of Land-Treatment Systems for Industrial Wastes", Ann Arbor Science, MI, (1979)

Comparison of the mass spectra for extractable organic fractions of waste, application area and control area indicated the possibility of persistence of one or more organic nitrogen compounds. These would be expected to undergo slow mineralization in the soil.

Turf grass grown in the application area showed significantly higher levels of copper than a similar crop grown in the control area. This did not affect the commercial value of the crop. Based on the observed levels in the turf grass, excessive copper concentrations in the food web through bioaccumulation are unlikely.

The site investigated is a commercial turf farm. Land treatment serves a dual purpose. First, it provides a convenient method of waste disposal to the waste generator. Second, it provides a supplimental source of lime to the turf farmer. The addition of lime, which is necessary to growing turf, also promotes immobilization of heavy metal constituents of this waste.

There is a pristine aquifer 20-30 feet beneath the surface of the land treatment/turf farm area. Although groundwater was not sampled in this study, the potential migration of soluble constituents or degradation products of the waste should be of concern. At the time of the field visits, water application rates were not mentioned and tended to be uneven. Records of when water has been applied in the past were spotty at best, and monitoring of environmentally significant waste components was not done.

RECOMMENDATIONS

Operational and managerial activities at the site should include:

- A more intensive site study (which includes groundwater monitoring) to assess the potential environmental impact.
- More study on the ability of the site soil to attenuate migration of metals and degrade organic species.
- Unsatturated zone monitoring of sodium to provide an early warning of migration to groundwater.
- Keeping records of application dates, waste characteristics, application procedures, and monitoring results.

SECTION 3

APPROACH

DATA COLLECTION AND ANALYSIS

Samples of the waste, baseline soil, and soil/waste mixtures were collected and analyzed for inorganic constituents and organic compound classes. Plants were collected and analysed to assess the extent of uptake of inorganic waste constituents.

The analytical protocol involved determining the following classical and inorganic waste parameters: pH, SO_4, and Cl^-, electrical conductivity (EC), cation exchange capacity (CEC), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V and Zn. Plasma emission spectroscopy and ion/chromatography were employed for inorganic species.

Analytical techniques employed for organic species included liquid chromatographic separation of organics into aliphatic, aromatic, and polar classes (LC-H, LC-A and LC-X, respectively), total chromatographic organics (TCO) and gravimetric (GRAV) analysis for volatile and non-volatile portions, and high resolution mass spectrometry (HRMS) for sorting classes by hydrogen saturation and heteroatom composition. The sampling and analytical methods are described in detail in the Appendix.

DATA INTERPRETATION

The analytical results from sampling the waste, the site receiving the waste, and a control site were compared to assess, insofar as possible, the relative decomposition, accumulation and migration of inorganic constituents and organic compound classes. The sampling and analytical program used in this study was designed to include sampling and analysis of appropriate control areas at the site so that any apparent concentration changes of waste components in application area samples could be differentiated from background levels. However, during preliminary site visits several factors were identified which would make it difficult to interpret any observed, apparent concentration changes. These factors include the following: an ideal control area was not available at the site; and, the chemical compositions of applied wastes were known to have varied over time.

The existence of many significant sources of uncertainty in the background data on the site made it desirable to provide some additional checks on the validity of the analytical data besides that provided by comparison of

TABLE 3. COMPARISON OF "TYPICAL" ELEMENTAL CONCENTRATION RANGES IN SOILS AND PLANTS WITH CORRESPONDING CONCENTRATION RANGES IN CONTROL AREAS USED IN THIS STUDY

Element	Typical Mean ppm Dry Soil (Range)[1]	Range ppm Dry Soil This Study[2]	Typical Range ppm Dry Plant Wt. Basis	Range ppm in Plant Ash This Study[5]
As	6 (0.1-40)	0.8-16	0.1-5[3]	1-16
B	10 (2-100)	2.1-9.2	5-30[3]	31-620
C	20,000	6,000-29,200	--	--
Ca	13,700 (7,000-50,000)	2,200-13,00	1,000-20,000	23,000-171,000
Cd	0.06 (0.01-0.7)	.3-.7	0.2-0.8[3]	1-4
Cr	100 (5-3,000)	7.9-65	0.2-1[3]	19-140
Cu	20 (2-100)	11-41	4-15[3]	69-290
K	14,000 (400-30,000)	2,300-8,400	20,400[4]	26,000-54,000
Mg	5,000 (600-6,000)	4,000-6,000	500-15,000[4]	14,000-40,000
Mo	2 (0.2-5)	1.7-3.3	0.2-5[3]	14-64
N	1,000 (200-2,500)	464-1,700	--	--
Na	6,300 (750-7,500)	22-440	--	940-10,000
Ni	40 (10-1,000)	9.6-31	10-10,000[4]	7-36
P	650	5,300-10,000	1,000-10,000[4]	17,000-168,000
Pb	10 (2-200)	24-280	0.1-10[3]	29-370
Se	7 (10-25)	0.1-0.5	0.1-2.0[3]	<.1-0.5
V	100 (20-500)	17-50	20-500[3]	3-90
Zn	50 (10-300)	41-110	10-300[3]	270-3,800

1. Bowen, H.G.M., Trace Elements in Biochemistry, Academic Press, Inc., NY, 1966.
2. CTL 0-6" Samples.
3. Allaway, W.H., Agronomic Controls Over the Environmental Cycling of Elements.
4. Berger, K.C., Sun Soil and Survival, University of Oklahoma Press, OK, 1976.
5. CTL Samples.

control and application area sample results. These checks are described below:

Inorganic Analysis

Validation of Control Samples --

The analytical data obtained in this study for control area samples from six landfarm sites are compared in Table 3 to typical concentration ranges found in soils and plants. Comparison of the soils data for the six sites indicates that almost all of the results obtained in this study are within typical concentration ranges. Exceptions are phosphorus (P), which was generally found in concentrations in excess of typical ranges, and sodium (Na) and selenium (Se), which were generally found in concentrations less than typical ranges. The selenium discrepancy may be due to volatilization of that element during the sample preparation procedure used in this study; the reasons for the sodium and phosphorus differences are not clear. Comparison of data on plants is of limited utility for several reasons, viz.: 1) plant uptake is species-specific; 2) uptake by a particular species is dependent on soil conditions; and 3) for the purpose of this study, elemental concentrations in plants have been expressed on an ash weight basis to compensate for the frequently poor physical condition of plants collected in the field. However, if we assume that the ash weight is usually on the order of 10% of the dry weight (the actual mean ash weight for all six control area samples in this study was 8.7% of dry weight), then the majority of results obtained in this study lie within typical ranges encountered in plants on a dry weight basis. In general, comparison of the results for control area samples in this study to typical elemental concentrations ranges in soils and plants suggests that there are no severe biases which would invalidate conclusions from the analytical data presented in this report.

Total Mass of Analyzed Parameters --

The sum of the masses of individual analyzed species in a sample of waste is a fraction of the total waste mass. For instance, if there were no species in the waste solids other than those determined in this study, the sum of all the individual masses should be approximately equal to 100%, depending on the uncertainty associated with the sampling and analytical methods. Inspection of the data presented shows that species determined in this study account for 68% of waste weight. The significance of this observation depends, of course, on the identity of the species that were not determined. Likely candidates are the elements Fe, H, O, Si and Al, all of which could be reasonably expected to occur in significant quantities in wastes of the type included in this study. In any case, consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Definition of Significant Pollutant Increases --

Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjelkahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area (APN/CTL).

Inspection of the data generated from six landfarm sites indicates that three elements - K, Mg, and P - show no significant increases above background, i.e., individual APN/CTL ratios for each of the elements at each site are close to 1.0 indicating that there is little difference in the actual concentrations of each of the elements between the APN and CTL area samples. The relative standard deviations of the mean APN/CTL ratios for these three elements are 33% (K), 9.1% (Mg), and 20% (P). Their mean relative standard deviation is approximately 20%; this number may provide a useful measure of the background variability of elemental concentrations in soils. Thus, for the purpose of this report, it has been assumed that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

The results for total metals, TOC and TKN in the wastes from all sites were used along with data obtained from the site owner on waste application rate (i.e., kg waste/acre/yr.) and waste percent solids, to estimate the number of years before one could expect to observe any increase of the elements analyzed in this study. The following assumptions were made:

1. Actual application rates have been the same as those given by the site operator;

2. All the waste generated for land treatment has been applied to the area which we sampled;

3. The waste has been incorporated uniformly into the top 12" of soil over the entire area described in #2; and

4. The waste composition has been constant and identical to that determined in this study.

The resulting estimates are discussed in more detail in chapter 4.

The steps in the procedure used to calculate the years of waste application necessary before one could expect to observe any increase above background were as follows.

Waste Application Rate --

The quantity kilograms of waste solids/acre/year was calculated from data supplied by the waste generator. For certain sites, the waste generator was able to provide an estimate of this quantity directly for other sites, where perhaps only an estimate of the annual volumetric waste generation rate was available, this calculation was performed according to the following equation:

$$\text{Kilograms of waste solids/acre/year} = \frac{\text{Annual volumetric mean generation} \times \text{Density of waste as applied} \times \text{\% solids in waste}}{\text{Acres of application area}}$$

In those cases where estimates of the waste density and % solids were not available from the waste generator, values obtained from laboratory analysis of waste samples collected during sampling visits to each site were used. As indicated in assumption 2 above, the value of the quantity "acres of application area" in the above equation was equal to the area in acres of the waste application area sampled in this study.

Annual Loading Rate of Individual Waste Species --
The quantity "kilograms of waste solids/acre/year" calculated in Step 1 was multiplied by the concentration in ppm of the element of interest determined in this study in waste samples collected from each site to give the annual loading of that element:

kg/acre/year x mg/kg (=ppm) of element of interest in waste solids = mg/acre/year

According to assumption 3, the waste was assumed to be incorporated uniformly into the top 12 inches of soil over the entire application area so the units of this quantity were assumed to be equal to mg/acre-foot/yr.

Annual Increase of Individual Waste Species --
The annual loading expressed as mg/acre/yr of each element of interest obtained in Step 2 was divided by an estimate of the average mass of one acre-foot of soil to give the predicted annual increase in concentration of each element of interest.*

Estimated Years of Waste Application --

The predicted annual increase in concentration of each element of interest was used to estimate the years of waste application necessary before one could expect to observe any increase above background of the elements analyzed in this study. The latter quantity depends on the detection limits of the sampling and analytical methods used for each element of interest. For example, the atomic absorption spectroscopic procedures used for analysis of many of the elements determined in this study involved digestion of ∿1.5 g of soil and dilution of the resulting solution to 50 milliliters. Assuming that our instrumental method was capable of detecting a change in concentration

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[The average mass of one acre-foot of soil was calculated as follows:

1 acre ∿ 43,560 ft^3; 1 acre-foot =
43,560 ft^3 x 1 ft = 43,560 ft^3;
43,560 ft^3 x .0283 m^3/ft^3 = 1233 m^3;
average bulk density = 1.6 g/cm^3 = 1.6 x 10^3 kg/m^3 (cf. Overcash, M.R. and D. Pal, Design of Land Treatment Systems for Industrial Wastes Theory and Practice, Ann Arbor Science, 1979);
1233 m^3 (1.6 x 10^3 kg/m^3) = 2 x 10^6 kg
Therefore,
(mg/acre-foot/yr) $\simeq$ 2 x 10^6 kg/acre-foot $\frac{\text{mg of element of interest (ppm/year)}}{\text{kg of soil-year}}$

of the element of interest in that solution equal to 1 part per million, the corresponding concentration change of that element in the soil sample taken for analysis would be ∿ 30 parts per million:

$$\left(\frac{1\mu g}{mL} \times 50\ mL\right) / 1.5\ g \approx 30\mu g/g = 30\ ppm\ in\ soil$$

The quantity ppm/year calculated in Step 3 was divided by 30 ppm to give the number of years of waste application necessary to observe a concentration change. Note that the "observable concentration changes" referred to here are not the same as "significant concentration increases" referred to in the preceding discussion.

For most elements determined in this study by atomic absorption (AA), the actual instrumental detection limit is probably lower than 1 ppm. However, since a systematic study of the detection limits of the combined sampling and analytical methods was beyond the scope of this study, the 1 ppm estimate may, in fact, be a more reliable estimate of the actual detection limits, given the uncertainty associated with the sampling methods.

Organic Data Interpretation

The principal objective of the organic chemical analysis program was to obtain data for a preliminary evaluation of the effectiveness of land treatment in degrading organic components of chemical wastes. To accomplish this objective it was necessary to characterize the organic components of the waste and to look for evidence of significant accumulation, degradation or migration of those components in the soil.

The organic analysis scheme provided for quantitative analysis of extractable volatile (TCO) and non-volatile (GRAV) organics, and of three polarity classes (LC-H, LC-A and LC-X) by liquid chromatography. Qualitative analysis of the organics by compound type was achieved by HRMS which provided data on heteroatom composition and the degree of compound saturation (R + DB values).

The combined qualitative and quantitative results provide insight into the extent of waste component degradation. For instance, an increase in polar species in APN area samples can be taken as an indication that the aromatic and aliphatic constituents originally in the waste have partially degraded since the byproducts of aerobic oxidation are generally polar oxygenated species. Typically, the organic analysis results do not permit determination of which waste components are being transformed into particular types of degradation products. However, the HRMS data do indicate which specific classes tend to persit in the soil column and which classes tend to appear as degradation products.

Accumulation of certain waste types can be determined by increases of aromatic and aliphatic classes relative to each other. For example, suppose the LC-H and LC-A fractions of extractable organics account for more than 50% of the organics in the APN 0-6 and 6-12 layers and in the control soil in

these fractions are only 10% of the total. The ratio of LC-A to LC-H in the waste is 0.24; in APN 0-6, 0.37 and in APN 6-12, 0.96. The absolute values of the LC-H and LC-A concentrations were lower in the APN 6-12 than in the 0-6. These types of trends are indicative of 1) preferentially degradation/or loss of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) in the APN soil compared to the CTL soil, without the appearance of oxidative degradation.

SECTION IV

RESULTS AND DISCUSSION

WASTE CHARACTERISTICS

The wastes being applied for land treatment are combined wastewater treatment sludges from clarifier and activated sludge lagoons of a batch organic chemical manufacturing facility (SIC Code 2865). Approximately 500,000 to 2,000,000 gallons of waste per year (wet basis) are generated and disposed of at the land treatment site. This waste is about 7% solids (93% water) as spread.

Total Mass of Parameters Analyzed

Data for the total amounts of all chemical species determined in waste solids from samples taken at the manufacturing facility in May 1978 are listed below.

	%
Metals	17.92
TOC	16.27
TKN	2.96
SO_4	0.34
Cl	0.0076
Total	37.5

The results indicate that species which could be reasonably expected to occur in significant quantities in this type of waste account for 37.5% of the total solids. Species not determined, include the elements Fe, H, O, Si and/or Al. Consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Inorganic Analysis

The results of analysis for total metals in the waste are presented in Table 4. Copper and zinc are present in the waste at relatively high concentration levels of 2000 μg/g and 1900 μg/g (dry weight) respectively. Other heavy metals such as cadmium, chromium, and lead are present in the waste.

These data from analysis of the waste were used along with data on waste application rate (2×10^6 gal/yr), waste density as applied (9.5 lbs/gal), and solids content of the waste as applied (7.0%) to estimate the years of waste application necessary before one could expect to observe any increase above

TABLE 4. INORGANIC WASTE ANALYSIS AND ESTIMATED YEARS FOR OBSERVABLE SOIL CONCENTRATION

Element	Waste Concentration (µg/g dried solids)	Estimated Years of Waste Application for Observable Soil Concentration Change
As	2	*
B	10	*
TOC	16.27%	1
Ca	7.4%	1
Cd	4.8	*
Cr	37	*
Cu	2000	2
K	1.8%	1
Mg	4.6%	1
Mo	8.9	*
TKN	2.96%	1
Na	2%	1
Ni	170	*
P	1.7%	1
Pb	100	*
Se	0.3	*
V	17	*
Zn	1900	2

*greater than 10 years

background levels of elements in the waste. We believe that the relative validity of the assumptions underlying these estimates (Section III) is high at this site. Table 4 shows the results of the calculation. It is seen that observable increases in the application area at the time of sampling would be expected for Ca, C, N, K, Na, P and Mg (in decreasing order of calculated concentration).

Organic Analysis

The waste was found to contain 96 mg/L of extractable organics. On the basis of the liquid chromatography (LC) separation of the extract, the organic materials were characterized as follows:

Aliphatic Hydrocarbons, non-volatile (GRAV):	9.5 %
Aromatic Hydrocarbons, non-volatile (GRAV):	3.6
Polar Organics, volatile (TCO):	1.8
Polar Organics, non-volatile (GRAV):	85.0 %

The recovery from the LC column for this sample was 65%. Thus, the above data have been normalized to 100%. Only 1.8% of the extractable organics will potentially be lost by volatilization.

The results of the HRMS analysis of the waste extract are presented in the R + DB summary matrix (Table 5). More than 85% of the material appears to be in R + DB categories 0-4. The ELCOMP assignments within each of these categories show series of low molecular weight (<150) ions that are most probably fragment ions formed from higher molecular weight waste components during analysis. If the mw<150 materials were present as such in the waste extract, they would have shown up in the TCO analysis, rather than the GRAV, because of their volatility.

The R + DB 0-4 hydrocarbon assignments are shown by ELCOMP to include ions up to $C_{10}H_{10}$, mw 140. Alkylbenzenes are likely components of R + DB 4. The predominant oxygen containing species are a series of fragment ions associated with fatty acids or esters and suggest that fatty acids/esters are major waste components.

The C, H, N species in R + DB 4 are dominated by an ion with ELCOMP assignment C_6H_7N. This is most likely an aniline or methyl pyridine fragment formed at the 300°C probe temperature. The R + DB 9, C,H,N category has a single ELCOMP assignment of $C_{14}H_8N_2$, probably also an ms fragment ion.

The waste extract R + DB matrix analysis also indicated a substantial quantity (20%) of material containing both a single oxygen and a single nitrogen atom. A 19% relative abundance rating was found for R + DB 4, C, H, N, O. The assignment was primarily due to one fragment ion, with an ELCOMP assignment of C_7H_9NO (mw 123.07). Based on matching of several other spectral peaks, this fragment was tentatively identified as a dimethyl- or ethylpyridone (hydroxypyridine) rather than a substituted aniline. The elemental composition C_7H_9NO is not commonly found in control soil samples. This may therefore have utility as a "tracer" for waste materials in the analysis of application area samples.

TABLE 5. R+DB SUMMARY MATRIX FOR WASTE SAMPLE*

R+DB	C,H	C,H,N	C,H,O	C,H,N,O	Total (from HRMS Analysis)
0					0
1	4.7	0.5	17.6	0.3	23.1
2	1.8	0.2	7.7	4.1	13.8
3	0.7	0.1	2.8		3.6
4	7.0	13.2	6.7	19.0	45.9
5	1.6	2.7	0.7	0.5	5.5
6	0.1	0.6	0.1	1.4	2.2
7	0.2	0.6	0.1		0.9
8					0
9		5.0			5.0

*All data in percent, normalized to 100%

In summary, the waste extractable organics appear to consist primarily of non-volatile polar materials. The HRMS analysis showed mainly low molecular weight (<150) ions that are probably fragment ions, representing aromatic C, H, N; C, H, O; and C, H, N, O compositions. Since parent ions of higher molecular weight homologs were not found, it seems probable that the actual waste components (from which the fragments are formed) are of sufficiently high molecular weight to be non-volatile at the 300° probe temperature.

SOIL CHARACTERISTICS

Inorganic Analysis

The application area sampled in this study was 39 acres in extent. On the order of 500,000-2,000,000 gallons of waste had been applied to the area for the first time in 1976, two years prior to our sampling visit. Inorganic analytical data on soils is presented in Table 6. Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjeldahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area. These "APN/CTL ratios' are also shown in Table 6. As discussed in Section III, for the purpose of this report it was judged that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than ±20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

These data from analysis of the waste (Table 4) were used along with data on waste application rate (2×10^6 gal/yr), waste density as applied (9.5 lbs/gal), and solids content of the waste as applied (7.0%) to estimate the years of waste application necessary before one could expect to observe any increase above background levels of elements in the waste. We believe that the relative validity of these assumptions underlying these esimates (Section III) is high at this site. Table 5 shows the results of the calculation. It is seen that observable increases in the application area at the time of sampling would be expected for Ca, C, N, K, Na, P and Mg (in decreasing order of calculated concentration).

Other elements, including those for which an observable increase above background was predicted, had an APN/CTL ratio 1.0. Comparison of APN 0-6" and APN 6-12" soil samples to CTL 0-6" and CTL 6-12" soil samples shows that these elements have apparently not been leached down into the soil, since there is no apparent proportional increase in the concentration of any of these elements in the APN 6-12" samples relative to the corresponding concentration changes in the CTL area samples. The relatively high level of copper in the APN 0-6" compared to APN 6-12" may indicate exchange, adsorption or precipitation in the upper soil layers. Data for pH, CEC, sulfate, chloride and electrical conductivity are given in Table 7. Increases in electrical conductivity in the APN 6-12 sample compared to the corresponding CTL 6-12" sample may indicate that those waste constituents which appear to increase in concentration in APN area soils may be present in those soils as soluble salts. These have the potential for being leached downward below the zone of incorporation.

TABLE 6. INORGANIC ANALYSIS OF CONTROL AND APPLICATION SOILS

Element	Concentration in Soils (µg/g dry wt.)				
	CTL		APN		
	0-6"	6-12"	0-6"	6-12"	APN/CTL*
As	16	9	12	8	0.8
B	2.1	2.4	1.0	1.0	0.4
TOC	2.92%	NA	1.45%	NA	0.5
Ca	2400	1600	2000	1500	0.9
Cd	0.3	-	0.3	0.3	2.0+
Cr	19	18	19	17	1.0
Cu	41	21	78	47	2.0
K	2300	2100	1300	1200	0.6
Mg	5200	5100	4700	4700	0.9
Mo	1.7	1.4	1.3	1.0	0.7
TKN	0.17%	NA	0.12%	NA	0.7
Na	28	26	20	18	0.7
Ni	9.6	13	9.4	9.5	0.8
P	7300	6600	5300	4900	0.7
Pb	27	18	15	12	0.6
Se	0.5	0.2	0.2	0.2	0.6
V	32	29	19	20	0.6
Zn	41	44	47	44	1.1

* = APN/CTL Ratio calculated as [APN (0-6) + APN (6-12)] / [CTL (0-6) + CTL (6-12)].

\+ = Absolute levels of Cd are too small to attach significance to this ratio.

TABLE 7. SITE SOILS: INORGANIC PARAMETERS

Sample	pH	C.E.C. meq/100g	E.C. µmhos	$SO_4^=$ µg/g	Cl^- µg/g
Waste Soil:				3400	76
CTL 0-6	5.7	10.2	200	260	22
CTL6-12	5.0	6.1	94	260	5
APN 0-6	6.0	6.9	168	220	13
APN 6-12	5.4	5.0	170	160	2

Organic Analysis

Based on data collected at three additional land treatment sites, the following composite picture of a "typical" sample, in terms of extractable organics, can be drawn:

> A control soil sample in this project typically contained ≤150 mg/kg of extractable organic material, all in the GRAV range, that was polar (> 80% in LC-X). The HRMS matrix analysis approach showed predominantly R + DB 1-4 hydrocarbons and oxygenates, with some R + DB 5-9 hdrocarbons and nitrogenous materials. Little or no material in the R + DB 10 range was present.

TABLE 8. QUANTITIES OF TOTAL AND EXTRACTABLE ORGANIC MATERIAL ON CONTROL SOIL SAMPLES

	Organic Material, mg/kg	
	Total organic carbon	Extractable organic
CTL 0-6"	29,200	140
CTL 6-12"	65	32

Table 8 presents data on the total organic carbon content and the quantity of extractable organic material in soil control samples. It is obvious that a small and highly variable portion of the soil organic material is extracted by methylene chloride. Known types of non-extractable organics include high molecular weight polymeric materials, such as amino acids. Non-polar and moderately polar organic species of molecular weights up to 500 or 1000 are generally efficiently extracted from environmental samples by methylene chloride. All of the extracted material is in the GRAV range (b.p. 300°C) which is expected, since TCO range organics (b.p. 100-300°C) would be lost from soil by volatilization. CTL 6"-12" samples have considerably lower levels of extractable organics than CTL 0"-6" samples as expected due to the decrease in the amount of soil organic matter with increasing soil depth.

The results of the HRMS analyses of the CTL 6-12" samples are generally quite similar to those of the corresponding CTL 0-6" samples, with slight shifts towards higher R + DB values and toward lower relative abundance of oxygenates (Figure 4).

The results of the LC separation of the CTL 0-6" sample extracts into aliphatic hydrocarbon (H), aromatic (A), and polar (X) fractions are presented schematically in Figure 1. The fractionation pattern shows polar materials to be dominant.

Figure 2 presents the LC fractionation results for the CTL 6-12" samples. The confidence level for these results is significantly reduced because of the small quantities of extracted organics actually available for LC. Nevertheless, the distributions observed are credible in comparison with its corresponding CTL 0-6" samples.

Figures 3 and 4 present a schematic overview of the R + DB summary matrices for the soil control samples. The R + DB summary matrix in each case is dominated by hydrocarbons (C,H) and oxygenates (C,H,O) in R + DB classes 1-4. The difference in profiles between Figures 3 and 1 is due to the fact that the R + DB matrix approach consistently and uniformly omits the paraffinic hydrocarbons (LC-H) and emphasizes the aromatic hydrocarbons (LC-A) compared to the polar species (LC-X). Hydrocarbons and nitrogenous compounds (C,H, N) in R + DB classes 5-9 are the next most abundant categories.

The application area 0-6" depth (APN-0-6) and 6-12" depth (APN 6-12) samples were found to contain 154 mg/kg and 81 mg/kg, respectively, of extractable organic material. These are not significantly higher than the corresponding values for the control samples: 140 mg/kg for CTL 0-6 and 32 mg/kg for CTL 6-12. Waste application to date, therefore, has not led to a signficiant accumulation of extractable organic materials in the soil. This could result either from low application rates or from complete degradation of waste components.

Figure 5 presents the results of the LC separation of the site application area samples, as well as those of the corresponding waste and control area samples. It is clear from the figure that all of the sample extracts wastes, APN, and CTL - show qualitatively similar LC fractionation patterns. For example, LC-X comprises 86% of the waste extract, 83% of the APN 0-6 extract and 85% of the CTL 0-6 extract. The LC data cannot, therefore, be used to detect oxidative decomposition of the waste. An apparent relative enrichment of aromatic hydrocarbons in APN 0-6 compared to the waste can be recognized as not significant by the fact that the CTL 0-6 sample also appears "enriched" in aromatics compared to the waste. For this waste and site, the LC data by themselves cannot be interpreted in terms of land treatment effectiveness.

In Figure 6 the R + DB cluster profiles, on a relative distribution basis, are plotted for the waste, APN 0-6, APN 6-12 and CTL 0-6 samples. Figure 7 presents similar profiles in which the R + DB data have been weighted to reflect the differences in the total quantities of extractable materials in the various samples.

The R + DB cluster profiles, like the LC fractionation patterns, reveal considerable similarities among the samples. Both the APN samples appear to be enriched in R + DB 1-4 C, H species compared to the waste, but the significance of this is unclear since the CTL 0-6 sample shows similar "enrichment." Since all the ELCOMP assignments in these categories represent fragments, and the fragments are the same in all five site samples, one cannot attribute significance to any of the apparent changes in the fine structure of R + DB matrix for the C, H compositions. An exactly analogous problem occurs for the C, H, O data; APN 0-6 and CTL 0-6 look more like each other, in general and in detail, than APN 0-6 looks like waste.

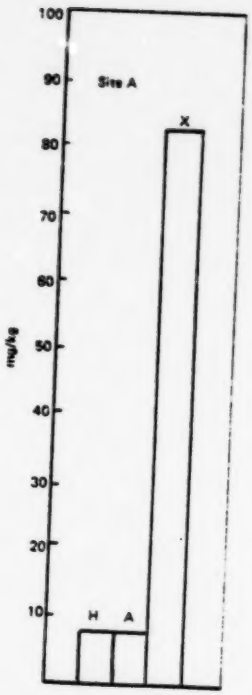

FIGURE 1 LC RESULTS FOR CTL 0-6 SAMPLES

Legend
X – Polar
A – Aromatic
H – Aliphatic

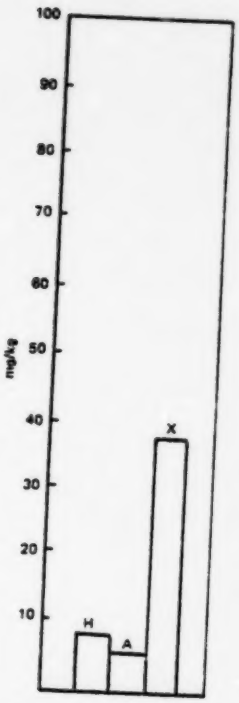

FIGURE 2 LC RESULTS FOR CTL 6-12 SAMPLES

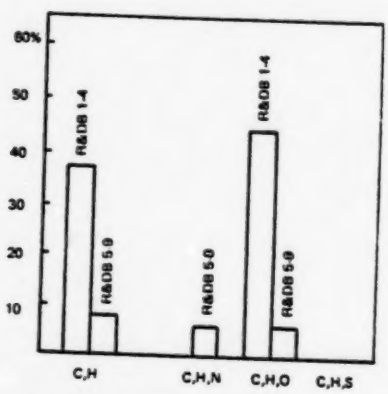

FIGURE 3 R&DB CLUSTERS FOR CTL 0-6 SAMPLES

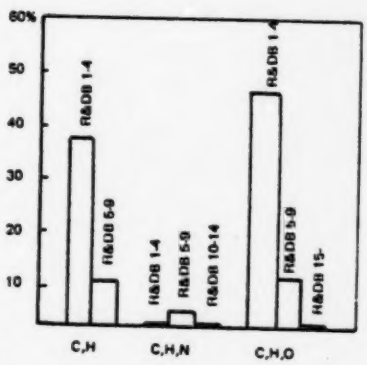

FIGURE 4 R&DB CLUSTERS FOR CTL 6-12 SAMPLES

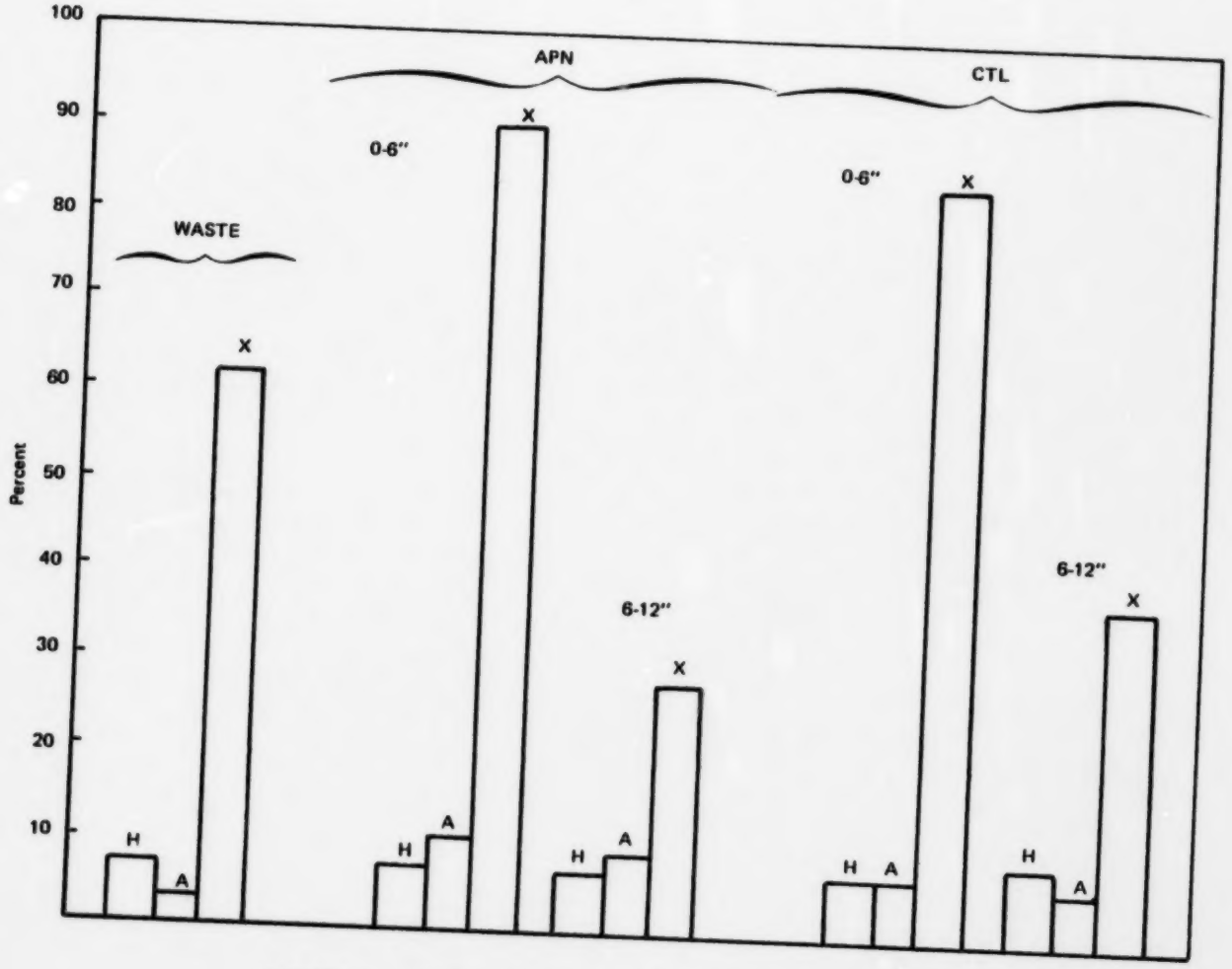

FIGURE 5 HISTOGRAM OF LC SEPARATION INTO ALIPHATIC (H), AROMATIC (A) AND POLAR (X) ORGANIC CLASSES

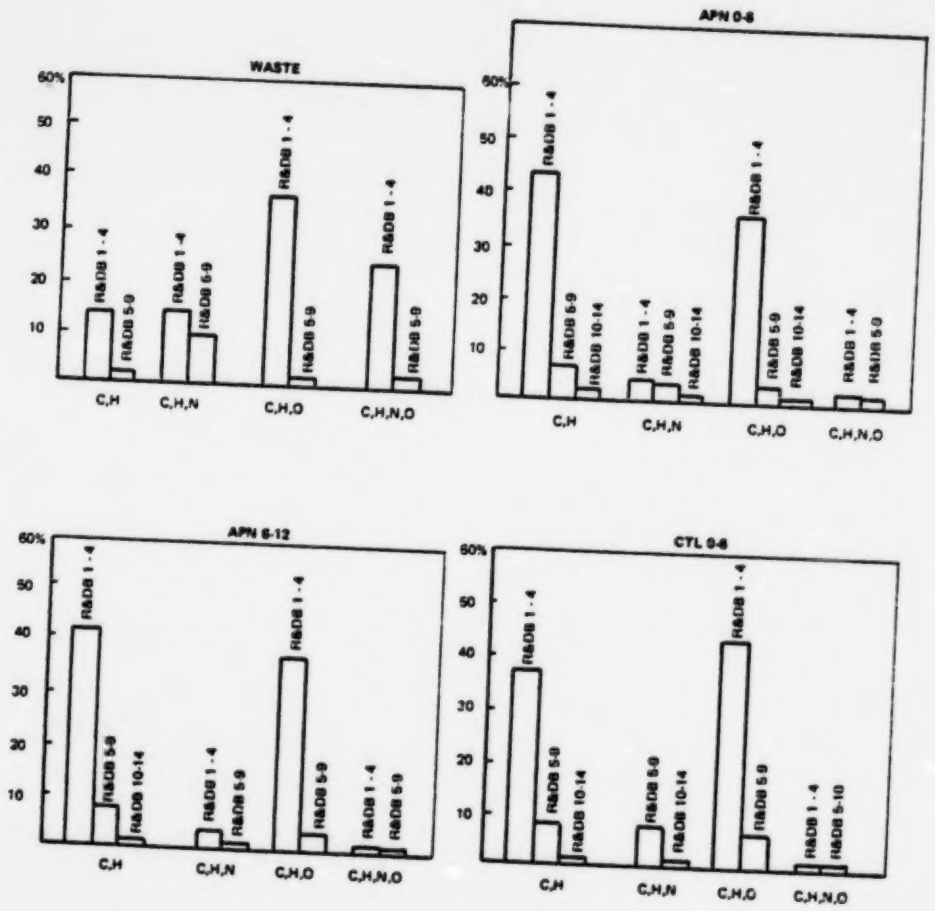

FIGURE 6 R+DB CLUSTER PROFILES, RELATIVE ABUNDANCE BASIS

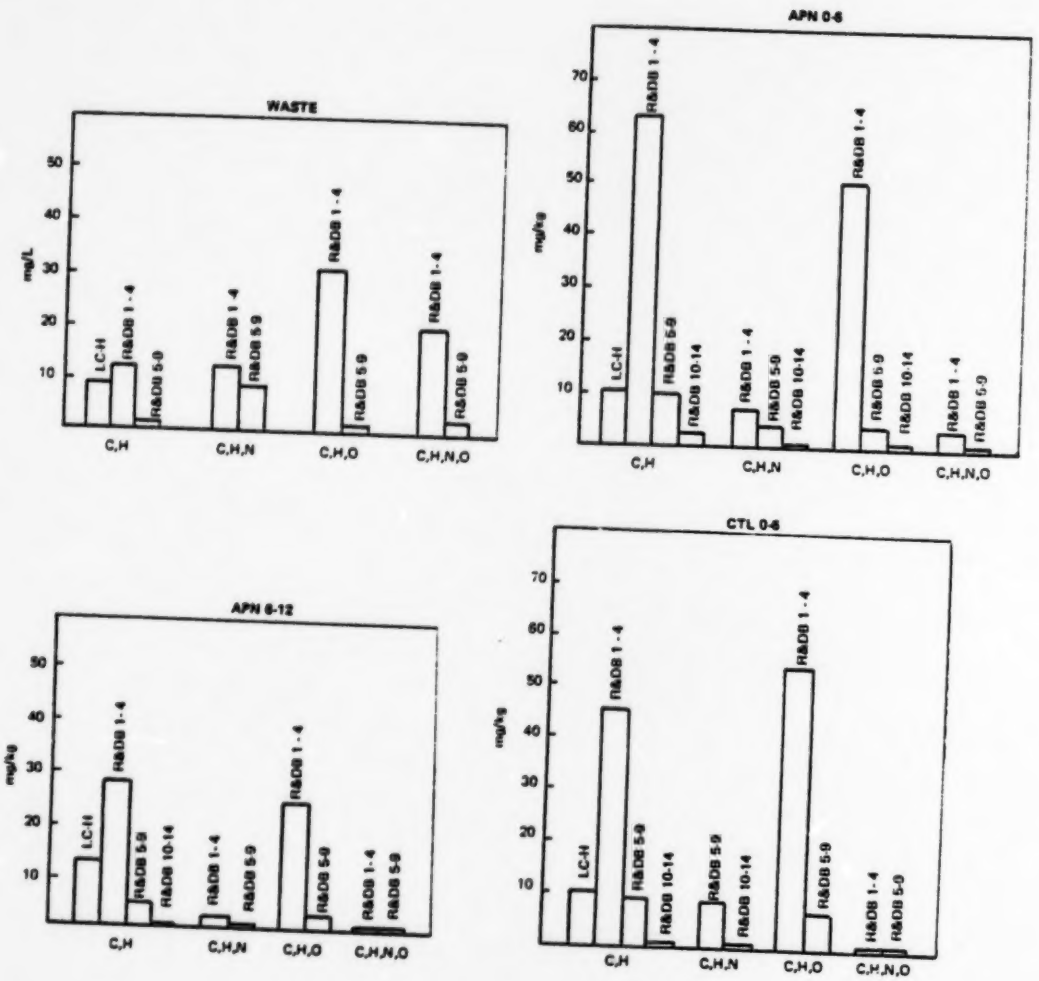

FIGURE 7 R+DB CLUSTER PROFILES, WEIGHTED BASIS

The HRMS data for the C, H, N and C, H, N, O compositions, provide some evidence for accumulation of waste components in the soil. The R + DB 1-4, C, H, N cluster for waste, APN 0-6 and APN 6-12 samples are dominated by the same ms fragment ion, identified as C_6H_7N by ELCOMP. This ms-fragment is not found in the CTL sample HRMS analyses. Its presence in the APN samples can, therefore, be attributed to the persistence of some waste components. Similarly, the C, H, N, O, R + DB 1-4 cluster in waste, APN 0-6 and APN 6-12 is dominated by the C_7H_9NO ms-fragment ion, based on ELCOMP assignments. That fragment is not found in the CTL samples.

In summary, waste application areas had low levels of extractable organic material, comparable to those of control areas, and the qualitative elemental composition of C, H and C, H, O materials was similar in waste, APN, and CTL samples. Therefore, no conclusions can be drawn concerning these components of the waste. There is some evidence that waste components, associated with C, H, N and C, H, N, O, R + DB 4 fragments in the HRMS analysis, have accumulated in the application area soils.

PLANT ANALYSIS

Two sets of composite turf grass samples (one APN, one CTL) were collected at the site for analysis. Soil and waste levels of the same constituents were compared with plant levels. The comparative values were examined in relationship to the cation-exchange capacity, pH and DTPA extractable metals in application and control area soils.

Results are given in Tables 9, 10, 11 and 12. It should be noted that plant analyses were based on ashed samples. It was decided that this procedure would be the most accurate due to the fact that plants were sampled at varying times during their respective growing cycles.

As indicated in Table 9*, concentrations of B, Ca, K, Mg, Mo, Na, P and Z were considerably lower in application area grass samples than in controls. In most of these cases (B, Ca, Mg, Mo and P) the lower levels in APN grass samples correspond to slightly lower soil levels. Also, comparison of the ratios of concentrations in plant ash to mean concentration in soil (cf. Table 12) indicates that concentrations of B, Ca, K, Mg, Mo and Na are slightly to considerably higher in plants compared to soil in the control area as well. The data reported for DTPA extractable elements (Table 10) do reflect the higher Mg levels (and possibly Zn). Soil pH, slightly more acid in the control area, could explain higher boron levels, but not the higher molybdenum levels. Based on this information and the single sampling effort, no conclusions can be drawn. In fact, such variability may be typical considering variations in plant, fertilization, liming rates, etc., between the control and application areas.

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*Any conversion of these results to a dry weight basis based on percent ash would be similarly elevated, and such calculated values would not be valid for these samples. Some decomposition of the grass samples, collected at Site A occurred prior to analysis, so that the dry weight of sample taken for analysis is not an accurate representation, resulting in exaggerated percent ash numbers.

TABLE 9. TOTAL ELEMENTS ANALYZED IN ASHED GRASS SAMPLES

Element	Concentration (μg/g) ash	
	CTL	APN
Ash	18.9%	41.6%
As	16	14
B	31	10
Ca	4.3%	1.1%
Cd	4	2
Cr	48	41
Cu	160	350
K	4.6%	5035
Mg	2.4%	5700
Mo	19	5
Na	1.0%	600
Ni	26	25
P	2.7%	1.0%
Pb	93	91
Se	<.6	0.5
V	45	44
Zn	3800	1700

TABLE 10. SOIL SAMPLES: DTPA EXTRACTABLE METALS

Element	Concentration (µg/g)			
	CTL		APN	
	0-6"	6-12"	0-6"	6-12"
As	NA	NA	NA	NA
B	0.2	0.1	0.1	0.2
Ca	NA	NA	NA	NA
Cd	0.1	<.1	<.1	<.1
Cr	0.3	0.1	0.1	0.1
Cu	12	4	29	16
K	10	-	-	-
Mg	46	14	35	10
Mo	-	-	-	-
Na	9	2	8	5
Ni	0.8	0.4	0.4	0.3
P	-	-	-	-
Pb	3	1	1	1
Se	NA	NA	NA	NA
V	0.9	0.5	0.7	0.2
Zn	2	1	1	1

TABLE 11. RATIOS OF APPLICATION AREA/CONTROL AREA FOR PLANT AND SOILS TOTAL ELEMENT CONTENT

Element	Grass Plants	Soil
	APN/CTL	APN/CTL
As	0.9	0.8
B	0.3	0.4
Ca	0.3	0.9
Cd	0.5	2.0
Cr	0.9	1.0
Cu	2.2	2.0
K	0.10	0.6
Mg	0.2	0.9
Mo	0.3	0.7
Na	0.1	0.7
Ni	1.0	0.8
P	0.4	0.7
Pb	1.0	0.6
Se	0.8	0.6
V	1.0	0.6
Zn	0.4	1.1

TABLE 12. RATIO OF PLANT ELEMENT CONCENTRATION (ASH WEIGHT)/ SOIL ELEMENT CONCENTRATION (MEAN OF DEPTHS)

Element	Plant/Soil Element Concentration Ratio	
	CTL	APN
As	1.28	1.4
B	13.8	10.0
Ca	21.5	6.3
Cd	∿2.7	6.7
Cr	2.6	2.3
Cu	5.2	5.6
K	21.0	4.0
Mg	4.7	1.2
Mo	11.9	4.3
Na	370.0	31.5
Ni	2.3	2.6
P	3.9	2.0
Pb	4.1	6.7
Se	∿1.7	2.5
V	1.5	2.3
Zn	89.4	37.4

The two metals of greatest interest at the site are copper and zinc. Increases in copper concentations in both the soil and plants were observed for the application area when compared with controls (Table 10). Higher levels of extractable copper were also observed in application area soil, although the application area is less acid, which should reduce Cu availability (compared to the control). Also the application area soil has a lower CEC which would suggest that Cu should be less well attenuated. It is possible that the increases observed may be due to waste application, although the single sampling effort makes such a conclusion very tentative.

Zinc levels in plants based on ash weight were lower at the application area compared to the controls. The degree of increase in plants at both areas compared to soils is of interest. Several hypotheses are possible (separately or in combination):

- Zinc may be present in fertilizers or other additives being used on the farm.
- Zinc may be less available at the application area due to competition with the elevated copper levels (although neither element exceeds the reported nationwide range of soil levels).
- Zinc levels reported for the top six inches of soil may be low due to zinc presence in the surface soil matted and removed with the grass sod and hence, not present to be analyzed in our samples.
- The control area may not be a true control, as definitive records of application were not available.

APPENDIX

METHODS OF SAMPLING AND ANALYSIS

DATA COLLECTION PROCEDURES

Several approaches were used to collect data from the six field sites selected for study. Information sources included published surveys such as those produced by the Soil Conservation Service and/or local universities and state agencies. Where feasible, information gathered from interviews with site or industry personnel along with site observations were utilized to confirm or adjust such information for location specificity.

FIELD SAMPLING

The field sampling and analysis program was designed to provide information on the following:

1. The rate and extent of waste degradation,
2. The migration of inorganic species,
3. The accumulation of waste constituents in the soil, and
4. Bioaccumulation of inorganic species in vegetation.

To this end, measurements were made of the concentration of various chemical species in soil and vegetation samples taken from waste application and control areas. The species selected for analysis were those that occur as a direct result of the land cultivation operation and/or transport of any constituents of the wastes.

Sampling Methods

Sampling Locations--

At each site, samples were taken from (1) the area where waste had been applied and (2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area

was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Sample Types--

The types and numbers of samples collected at each site included at a minimum the following:

	Control Area	Application Area
1) Waste	1 Sample	
2) Soil	2 Samples	2 Samples
3) Soil-Waste Mixture	-	2 Samples
4) Vegetation	1 Sample	1 Sample

Core samples of soil and soil-waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered, and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There were no opportunities for sampling surface water, runoff, or groundwater at any site during the sampling visits made.

CHEMICAL ANALYSIS

Inorganic

Analyses of inorganic parameters were conducted on the waste samples, soil and soil-waste mixture composite samples from application and control areas, and vegetation composite samples from application and control areas. Analytical methods used for determination of inorganic parameters are shown below. DTPA-Extractable metals are those metals which may be available for biological uptake.

Parameter	Method
B, Cu, Cd, Cr, Cu, K	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
Mg, Mo, Na, Ni, P, Pb, V, Zn	
As, Se	Hydride evolution, atomic absorption spectroscopy

Total Organic Carbon (TOC)	Combustion, gravimetric
Total Kjeldahl Nitrogen (TKN)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (CEC)	Volumetric
Electrical Conductivity (EC)	Conductivity Meter
pH	pH Meter
DTPA-extractable metals	DTPA extraction, plasma emission spectroscopy

Organic

The organic analysis scheme is shown schematically in Figure 8. The methodology involved:

1. Solvent extraction with methylene chloride;
2. Quantitative analysis of volatile and non-volatile organics;
3. Liquid chromatographic separation of the extracts to divide the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons, and polar species; and
4. Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

Each of the steps of the methodology is described in further detail below.

Extraction--

The method adopted for isolation of organic components from the waste and soil samples was extraction with methylene chloride. Methylene chloride is a solvent which gives high extraction efficiency for a wide range of organic compound types. In particular, it is generally effective for non-polar and moderately polar, hydrophobic organics, which are the types of compounds that dominate many current lists of compounds of concern. It should be recognized, however, that polymeric, humic, proteinaceous materials, very polar, water-soluble, or soil-bound species will not be efficiently extracted. It should also be noted that these non-extractable species, if isolated, would generally not be amenable to available analysis techniques. An organic compound which is extractable from a waste sample may not be extractable from a corresponding soil sample because of soil bonding. Since non-extractable organics are probably less likely to be transported into plant cells, they may be of less environmental concern.

Control and application area soil samples (ca 100 g) were Soxhlet extracted with methylene chloride (ca 200 mL) for 24 hours. Waste samples were

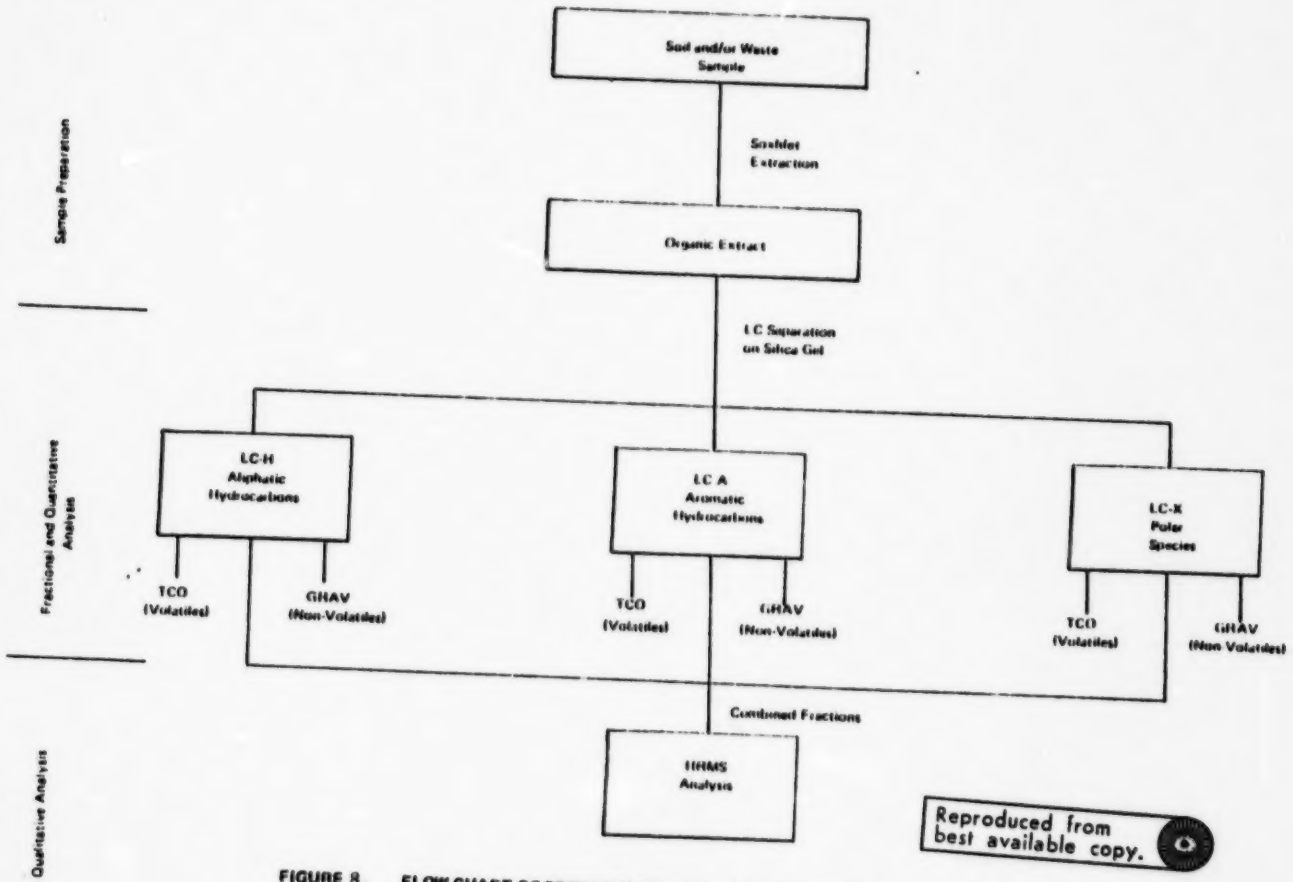

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FIGURE 8. FLOW CHART OF PROPOSED ORGANIC ANALYSIS SCHEME

subjected to Soxhlet extraction, or to liquid-liquid separatory funnel extraction (3 times 100 mL of solvent per liter of waste), depending on their physical state. The methylene chloride extracts were concentrated to 10 mL final volume by use of Kuderna-Danish evaporative concentrators.

Quantitative Analysis--

Total Chromatographable Organics (TCO)--The Total Chromatographable Organics (TCO) analysis is a gas chromatographic (GC) analysis procedure that uses a flame ionization detector. A 1-5μL aliquot of the sample is injected. Resolution of individual QC peaks is not intended. The total integrated detector response is used to derive a single estimate (mg) of the quantity of material in the 100-300°C boiling point range.* The detection limit for a complex sample mixture is on the order of 50 ppm (w/v) in the solution injected. This corresponds to 0.5 mg total in the 10 mL sample extract.

Gravimetric Analysis (GRAV)--The GRAV procedure is a quantitative analysis of non-volatile components (materials above 300° boiling point range) of the sample extract. An aliquot of the organic solution is evaporated to constant weight, over silica gel, in a tared weighing dish. The practical detection limit is on the order of 0.1 mg in the 1 mL sample taken for GRAV analysis. This corresponds to 1 mg total in the 10 mL sample extract.

Liquid Chromatographic Separation--

A liquid chromatographic (LC) separation on silica gel was used to separate the extracted organics according to polarity. This is a lowresolution technique that has been demonstrated at Arthur D. Little, Inc. to provide reliable separation of organic components into three classes as indicated below.

LC-H: Aliphatic Hydrocarbons

LC-A: Aromatic Hydrocarbons

LC-X: Polar Organics (oxygenates, amines, etc.)

Details of preparation of the silica gel LC column have been published. The methylene chloride extracts were applied to the column after solvent exchange into cyclohexane. The elution sequence used in this program was as follows:

LC-H: 15 mL of pentane

LC-A: 15 mL each, sequentially, of 20% methylene chloride in pentane; 50% methylene chloride in pentane; and methylene chloride

* Arthur D. Little, Inc., studies using model compounds have shown that n-hexadecane (b.p. 303 C) defines a reasonable break point between TCO and GRAV range materials.

LC-X: 5 mL each, sequentially, of 5% methanol in methylene chloride; 20% methanol in methylene chloride, and 50% methanol in methylene chloride.

Each fraction was analyzed by TCO and TRAV procedures as described above. The fractions were then recombined prior to HRMS analysis.

The LC procedure was originally scaled for 15-100 mg samples applied on column. However, the total amount of material available for some samples in this program was 10 mg. Quantitative recovery from the column was 70-100% when samples containing about 10 mg or more were used, but 50% for very small samples.

The reproducibility of the extraction and LC separation for these samples was checked by running duplicate LC columns on a site application area soil extract. The results are shown in Table 13.

High Resolution Mass Spectrometry--

High resolution mass spectra were obtained on the recombined LC fractions for each of the landfarm sample extracts. A Dupont (CEC) 21-110 B high resolution mass spectrometer, using a glass inlet and solids probe for sample introduction, was employed. Spectra were recorded on photoplates. The basic spectral data were then obtained by a photoplate reader and the position and intensity of the lines transferred directly to a laboratory data system (LDS). This is the HIRES output. The LDS, based on a Data General Elipse S/200 computer, was used for subsequent HRMS data processing.

The high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e (mass-to-charge ratio). The high accuracy and precision makes it possible to take advantage of the mass defect characteristics of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all "plausible" combinations of elements corresponding to a given mass. "Plausible" combinations are defined by the analyst, based on a preliminary manual examination of the HIRES data. The objective is to allow all of the elemental compositions (C + H; C + H + S; C + H + Cl, etc.) that are necessary to characterize the range of the sample chemistry, but to minimize the computation time and the number of incorrect, "near-miss" match assignments. The theoretical and measured masses are next compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 atomic mass units. This information constitutes the ELCOMP output.

The ELCOMP output listing normally includes 400 to 1000 lines detected in the spectrum, their intensities, and 500 to 2000 associated chemical composition data. The approach used for interpreting this large quantity of data was to sort the assigned elemental composition into classes according to heteroatom composition (i.e., C,H; C,H,O; C,H,N; C,H,S) and degree of hydrogen unsaturation indicated by rings and double bonds. The R + DB value provides a convenient means of organizing data into probable chemical compound categories. Some examples will illustrate this point:

TABLE 13. REPLICATE EXTRACTIONS AND LC SEPARATIONS ON A SITE SOIL SAMPLE

	% Water	Dry Wt. Extracted (kg)	Extract			
			TCO (mg)	GRAV (mg)	Total (mg)	Total (mg/kg)
Before LC Fractionation						
Sample 1: APN 0-6	15.9	0.0966	ND	9.0	9.0	93.2
Sample 2: APN 0-6	15.6	0.1090	ND	8.0	8.0	73.4
After LC Fractionation						
Sample 1: APN 0-6						
LC-H			0.82	1.67	2.49	25.8
LC-A			0.39	1.17	1.56	16.1
LC-X			ND	4.00	4.00	41.4
						83.3
Sample 2: APN 0-6						
LC-H			ND	1.17	1.17	10.7
LC-A			1.30	0.50	1.70	15.6
LC-X			ND	5.30	5.30	48.6
						74.9

for an n-paraffin, C_6H_{14}, R + DB = 0

for phenol, C_6H_6O, R + DB = 4

for benzothiophene, C_6H_6S, R + DB = 6

for anthracene, $C_{14}H_{10}$, R + DB = 10

for benzopyrene, $C_{20}H_{12}$, R + DB = 15

All paraffins or other saturated species such as acyclic alcohols and sulfides will always be in R + DB group 0. A species must have an R + DB value of 4 or more to be aromatic, and R + DB value of 7 or more to be a naphthalene, an R + DB value of 8 or more to be a polychlorinated biphenyl (PCB), and so on. The R + DB values were grouped in this report as follows: R + DB = 0, 1 R + DB 4; 5 R + DB 9; 10 R + DB 14; and 15 R + DB.

Similar calculations can be made for any species of interest. This approach does not differentiate among the different isomers of any compound class, such as anthracene and phenanthrene, in R + DB 10.

The R + DB and elemental composition values were then used to sort all of the data from HRMS analysis into a compact matrix first according to the R + DB value and second according to the elemental composition of each of the ions identified. This approach presents a simple view of the overall composition of a sample from a highly complex spectrum. This approach requires that all ions finally included in the matrix are parent (molecular) ions. However, a large number of fragment ions in the spectra complicates the analysis. In interpreting the HRMS data it is also necessary to account for isotope ions (e.g., ^{13}C and ^{37}Cl), and composition assignments with large experimental errors. Consequently, in developing the R + DB matrix, certain restrictions were applied in an attempt to eliminate interferences and questionable calculated compositions. The restrictions applied were:

Molecular Weight: Ions below 90 atomix mass units were excluded to minimize the interference from fragment ions.

Error: Calculated compositions which differed from measured values by more than 2 millimass units were excluded.

Isotopes: All calculated compositions that included isotopes such as ^{13}C, ^{34}S, and ^{37}Cl were excluded.

R + DB: Only compositions with integral R + DB values were included, thus excluding fractional R + DB values which arise from fragment ions.

Carbon No.: A minimum carbon number limit was set for each R + DB class.

For this report, the individual intensities of all ions within each R + DB and element group were summed to give a single estimate of the abundance of that group. For each composite sample, these estimates were subsequently displayed in a condensed form as shown in Figure 9.

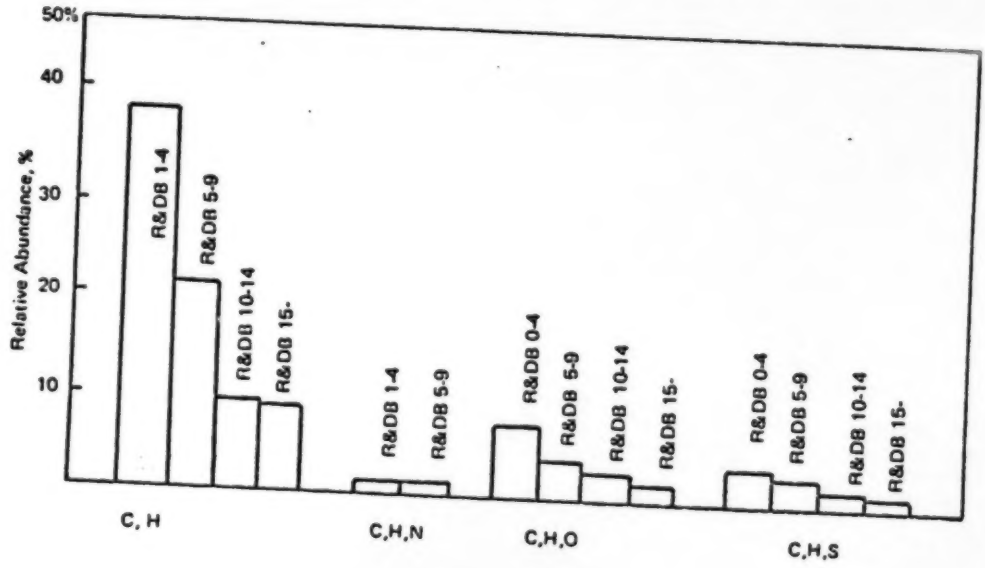

FIGURE 9. EXAMPLE OF DISPLAY OF R&DB AND ELEMENTAL COMPOSITION GROUPINGS FOR A SOIL SAMPLE EXTRACT